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Silicon Electrodeposition in a Water-Soluble KF–KCl Molten Salt: Utilization of SiCl₄ as Si Source

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The electrodeposition of Si was investigated in a molten KF–KCl salt mixture (eutectic composition, 45:55 mol%) after the introduction of SiCl₄ to demonstrate a new production method for solar cell substrates. Gaseous SiCl₄ was introduced directly into the molten salt at 1023 K by a vapor transport method using Ar as a carrier gas. The dissolution efficiency of SiCl₄ exceeded 80% even when a simple tube was used for bubbling. Galvanostatic electrolysis was conducted at 923 K on a Ag substrate at 155 mA cm^{−2} for 20 min in the molten KF–KCl salt mixture after the dissolution of 2.30 mol% SiCl₄. Although a compact Si layer was formed, its smoothness was inferior to that obtained from the melt after the addition of K₂SiF₆. The molar fraction of the fluoride anion is suggested as one of the factors affecting the morphology of the deposits.

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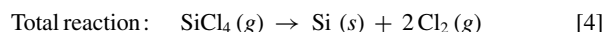
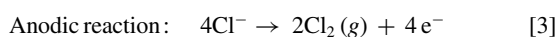
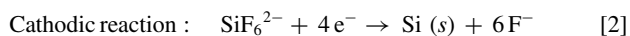
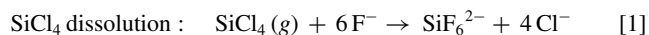


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The current production method for the Si substrates used in photovoltaic cells consists of multiple processes, including a slicing step of the high-purity Si ingots produced by the Siemens process. This method has several drawbacks in terms of energy efficiency and yield because of the low productivity of the Siemens process and the considerable kerf loss in the slicing step. Thus, the development of an alternative efficient process for manufacturing crystalline Si substrates is necessary to enable significant improvements for the photovoltaic industry.

The direct formation of Si films has been investigated as one of the alternative methods for producing polycrystalline Si solar cells. The electrodeposition of crystalline Si using high-temperature molten salts has been reported by several researchers since the 1970's.^{1–10} The use of fluoride-based molten salts, such as LiF–KF and LiF–NaF–KF, is effective for obtaining compact and smooth Si films.^{1,2,5,9,10} However, previous investigations that employed fluoride-based molten salts found that the low solubility of LiF and NaF in water makes the removal of the salt that adheres to the deposited Si a major problem.^{10,11} Another essential problem is the lack of high-purity and low-cost Si sources, on which the process previously studied was based. Conventionally, either K₂SiF₆ or the anodic dissolution of a Si rod was utilized as the supply of Si ions. However, the low-cost preparation of K₂SiF₆ and Si rods of solar-grade purity is difficult.

We proposed and investigated a new electrodeposition process for the formation of Si films from a molten KF–KCl electrolyte with high-purity gaseous SiCl₄ as a Si source (Fig. 1), with the aim of developing a new method for the production of polycrystalline Si films for solar cells.^{12–14} In this process, gaseous SiCl₄ is dissolved into the molten salt to form Si(IV) complex ions. Si films are then electrodeposited onto the cathode of an appropriate substrate, and Cl₂ gas is evolved at a carbon anode. The salt that adhered to the Si deposit is easily removed by washing with water.



In this process, Si electrodeposition is achieved without the introduction of impurities or changes in the composition of the molten salt. Moreover, halogen recycling is realized by recovery of the Cl₂ gas by-product, which can be used for chlorination of Si to produce SiCl₄. One advantage of our proposed process is the high solubility of the solidified KF–KCl salt in water (the solubilities of KF and KCl are 101.6 and 35.9 g, respectively, per 100 g H₂O) compared to other fluoride salts (the solubilities of LiF, NaF, MgF₂, and CaF₂ are 0.13, 4.15, 0.13, 0.0016 g, respectively, per 100 g H₂O).¹⁵ This molten salt is a unique fluoride-containing electrolyte with high water solubility, and the presence of fluoride during electrolysis is essential to obtain compact and smooth Si films. We have previously investigated the

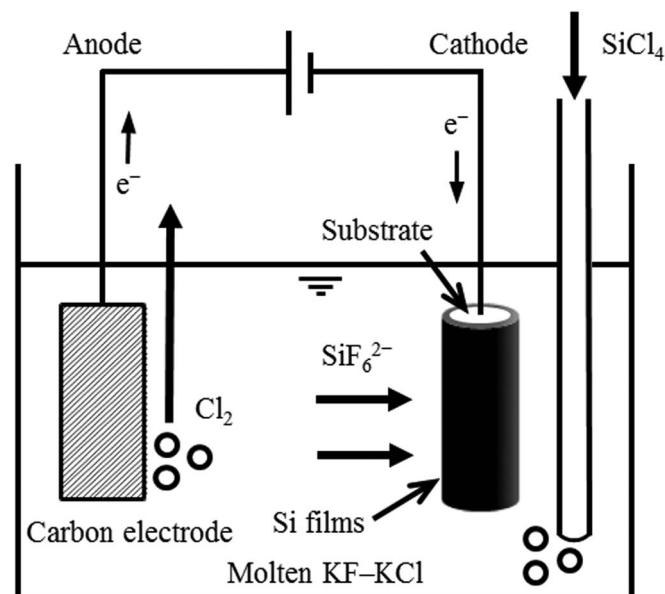


Figure 1. A schematic illustration of the principle of electroplating process of Si in KF–KCl molten salt.^{12,13}

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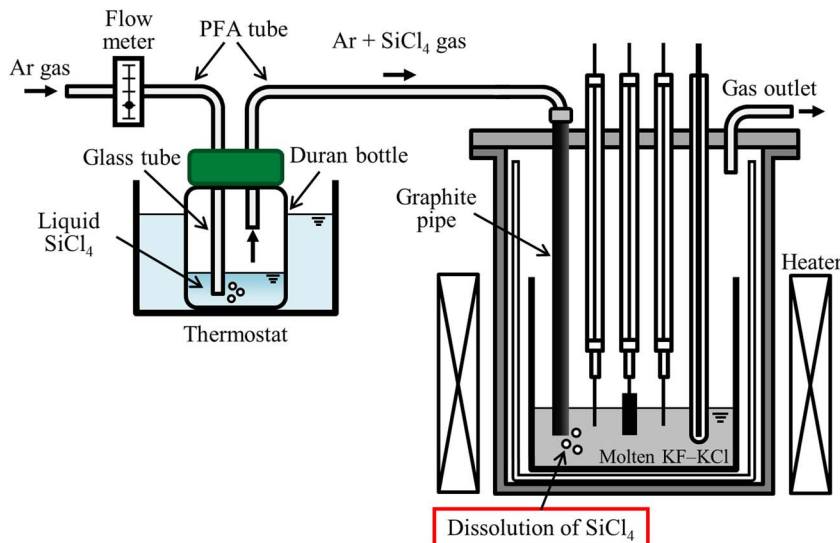


Figure 2. A schematic drawing of the experimental apparatus for the introduction of SiCl₄ by a vapor transport method.

electrodeposition of Si from Si(IV) complex ions on a Ag electrode in a molten KF–KCl–K₂SiF₆ system at 923 K as the first step of research, without the use of SiCl₄ gas.^{12–14} The Si films electrodeposited from a molten salt containing 0.5–5.0 mol% K₂SiF₆ exhibited adherent, compact, and smooth characteristics. Also, the residual salt on the deposited Si was easily removed simply by soaking in water.

In the present study, we investigate the feasibility of the use of SiCl₄ gas as a Si source. Gaseous SiCl₄ was introduced into molten KF–KCl by a vapor transport method using Ar as the carrier gas. The electrodeposits were obtained by galvanostatic electrolysis of the melt. The deposited Si was analyzed by cross-sectional scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

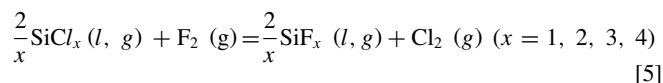
Experimental

The experimental setup is schematically illustrated in Fig. 2. Reagent-grade KF (Wako Pure Chemical Co. Ltd., >99.0%) and KCl (Wako Pure Chemical Co. Ltd., >99.5%) were mixed to form a eutectic mixture (45 mol% KF + 55 mol% KCl, melting point = 878 K¹⁶) and loaded in a graphite crucible (Toyo Tanso Co. Ltd., o.d.: 90 mm, i.d.: 80 mm, height: 120 mm). The mixture in the crucible was first dried under vacuum at 453 K for 72 h to remove residual moisture. The crucible was placed at the bottom of a quartz vessel in an air-tight Kanthal container with a stainless-steel lid. The salt was further dried under vacuum at 673 K for 24 h. The experiments were conducted in a dry Ar atmosphere at 923 K or 1023 K. Liquid SiCl₄ (Aldrich, 99.998%) held in a Duran bottle (100 mL) was maintained at 293 K in a water bath using a thermostat (As-one, Cool Circulator CH-202). Pyrex pipes (o.d.: 6 mm, i.d.: 4 mm) connected to perfluoroalkoxy alkane (PFA) tubes (o.d.: 6.35 mm, i.d.: 4.35 mm) were attached to the screw cap (As-one, pipe diameter: 6–8 mm) of the bottle. The mixed Ar–SiCl₄ gas was prepared by bubbling Ar gas (20 mL min^{–1}, Kyoto Teisan, Inc., >99.998%) into liquid SiCl₄ using a Pyrex pipe. The mixed gas was bubbled into the molten eutectic KF–KCl (200 g) at 1023 K with a graphite pipe (Toyo Tanso Co., Ltd., ISO-68TS, o.d.: 12 mm, i.d.: 5 mm, length: 470 mm). After bubbling the mixed gas for the predetermined period, the lower end of the pipe was removed from the melt and the flow gas was switched to pure Ar. Then, the temperature of the melt was lowered to 923 K, at which the electrochemical measurements were carried out. The working electrodes were Ag wire (Nilaco Corp., diameter: 0.1 mm, 99.98%) and Ag flag electrodes (Nilaco Corp., thickness: 0.1 mm, 99.98%).¹³ A glass-like carbon rod (Tokai Carbon Co., Ltd., diam.: 5.0 mm) was used as the counter electrode. A Pt wire (Tanaka Kikinzoku Kogyo, >99.95%, diameter: 1.0 mm) was employed as a quasi-reference electrode. The potential of the reference electrode was calibrated with reference to a

dynamic K⁺/K potential, which was prepared by the electrodeposition of metallic K on a Ag wire. The electrolyzed samples were soaked in hot distilled water at 333 K for 24 h to remove the salt adhered to the deposits and dried under vacuum for 12 h. The samples were analyzed by SEM (Keyence Corp., VE-8800) and EDX (AMETEK Co. Ltd., EDAX Genesis APEX2). For cross-sectional SEM observations, the samples were embedded in acrylic resin and polished with emery paper and buffing compound.

Thermodynamic Calculation

Figure 3 shows the Gibbs energies for the reactions of the chlorides with fluorine gas to form the fluorides and chlorine gas.¹⁷



As indicated in the figure, the Gibbs energy change for the formation of SiF₄ and Cl₂ from SiCl₄ and F₂ is much more negative than for the reaction of KF + Cl₂ to form KCl + F₂. Thus, the

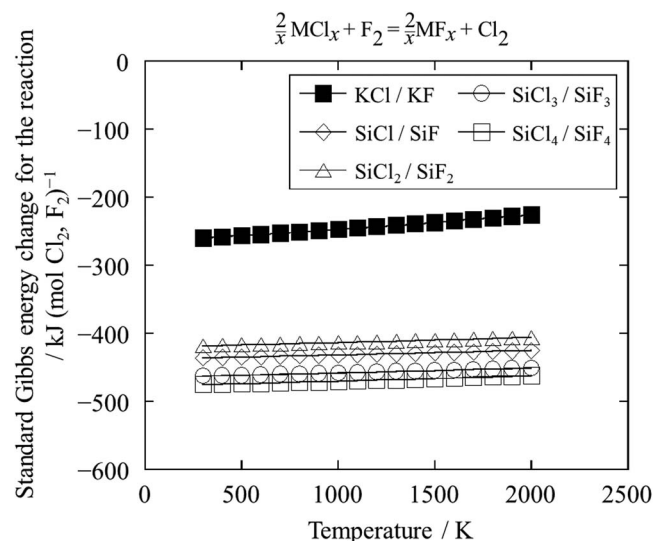
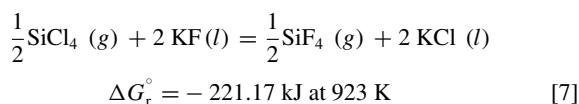


Figure 3. The standard Gibbs energy changes for the reactions of chlorides and F₂ gas to form fluorides and Cl₂ gas.¹⁷

conversion of SiCl_4 to SiF_4 in the reaction with KF is thermodynamically favorable.¹⁷



These thermodynamic calculations suggest that the SiCl_4 gas introduced into the KF-KCl melt is expected to dissolve to produce SiF_6^{2-} complex ions, which are highly stable in molten salts.



Results and Discussion

Vapor transport of SiCl_4 .—The SiCl_4 was supplied via a vapor transport method utilizing Ar as a carrier gas and the apparatus shown in Fig. 2. The flow rate of Ar gas and the partial pressure of SiCl_4 in the mixed Ar- SiCl_4 gas were used to modulate the vapor transport rate, and these factors were controlled using a gas flow meter and a thermostat, respectively. The vapor pressure of SiCl_4 , P_{SiCl_4} , is determined by the temperature, T , according to the following equations.¹⁸

$$P_{\text{SiCl}_4} = 10^{\left(4.0977 - \frac{1200}{T-37}\right)} \quad (275 < T < 330 \text{ K}) \quad [10]$$

In the present experiment system, the total gas pressure was 1 atm,

$$P_{\text{Ar}} + P_{\text{SiCl}_4} = 1 \text{ atm} \quad [11]$$

where P_{Ar} is the partial pressure of Ar. Thus, the flow volume rate of SiCl_4 , f_{SiCl_4} , is expressed as a function of the flow volume rate of Ar, f_{Ar} , at 298 K.

$$f_{\text{SiCl}_4} = f_{\text{Ar}} \cdot \frac{P_{\text{SiCl}_4}}{P_{\text{Ar}}} = f_{\text{Ar}} \cdot \frac{P_{\text{SiCl}_4}}{1 - P_{\text{SiCl}_4}} \quad [12]$$

Thus, the transport rate of SiCl_4 , v_{SiCl_4} , is

$$v_{\text{SiCl}_4} = \frac{P_0}{RT} \cdot f_{\text{SiCl}_4} = \frac{P_0}{RT} \cdot \frac{P_{\text{SiCl}_4}}{1 - P_{\text{SiCl}_4}} \cdot f_{\text{Ar}} \quad [13]$$

where R is the gas constant, and P_0 is the ambient atmospheric pressure ($1.013 \times 10^5 \text{ Pa}$).

The above relationships are valid only when the gas is ideal, and the evaporation is fast enough to reach equilibrium. The validity of these conditions was confirmed by flowing Ar gas (20 mL min^{-1}) into liquid SiCl_4 for 50 min at 293 K, where the value of P_{SiCl_4} is 0.257 atm, and measuring the resulting weight change. The transport rate of SiCl_4 , v_{SiCl_4} , is calculated from Eqs. 14 and 15.

$$W_{\text{SiCl}_4, \text{trans}} = W_{\text{SiCl}_4, \text{bef}} - W_{\text{SiCl}_4, \text{aft}} \quad [14]$$

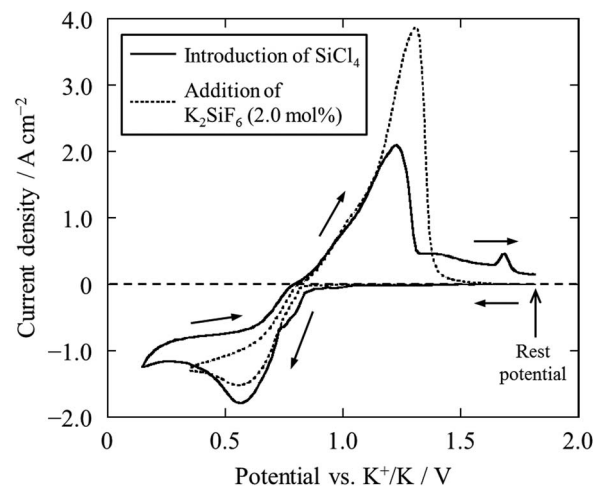


Figure 4. Cyclic voltammograms for a Ag flag electrode in molten $\text{KF-KCl-K}_2\text{SiF}_6$ (2.0 mol%) at 923 K and molten KF-KCl at 923 K after the introduction of SiCl_4 . Scan rate: 0.50 V s^{-1} .

$$v_{\text{SiCl}_4} = \frac{W_{\text{SiCl}_4, \text{trans}}}{M_{\text{SiCl}_4} \cdot t} \quad [15]$$

Here, $W_{\text{SiCl}_4, \text{bef}}$ and $W_{\text{SiCl}_4, \text{aft}}$ represent the total weight of liquid SiCl_4 and Duran bottle before and after the Ag gas flow, respectively. The value of $W_{\text{SiCl}_4, \text{trans}}$ shows the weight of SiCl_4 transported during the experiment. As shown in Table I (Exp. #VT-1), the experimental value of v_{SiCl_4} was calculated to be $2.86 \times 10^{-4} \text{ mol min}^{-1}$ from $W_{\text{SiCl}_4, \text{trans}} = 2.43 \text{ g}$ and Eq. 15. The theoretical value of v_{SiCl_4} from Eq. 13 is $2.83 \times 10^{-4} \text{ mol min}^{-1}$. A good agreement between experimental and theoretical values confirms that the present vapor transport method provides precise control of the SiCl_4 supply.

Injection of SiCl_4 into molten KF-KCl .—In our previous study, K_2SiF_6 concentrations of 2.0–3.5 mol% and current densities of 50–200 mA cm^{-2} at 923 K were determined to be the optimum conditions for the electrodeposition of adherent, compact, and smooth Si layers in molten $\text{KF-KCl-K}_2\text{SiF}_6$.¹⁴ Thus, we injected 2.86 mol% of SiCl_4 (with respect to the eutectic KF-KCl salt) by bubbling with the mixed Ar- SiCl_4 gas. Thus, 14.90 g of gaseous SiCl_4 was transported from the liquid SiCl_4 to 200 g of the KF-KCl melt at 1023 K. As shown in Table I (Exp. #VT-2), there is good agreement between the experimental and theoretical transport rates, which was $2.83 \times 10^{-4} \text{ mol min}^{-1}$.

After the injection of SiCl_4 , the bath temperature was lowered from 1023 K to 923 K, and the melt was investigated by cyclic voltammetry. The solid line in Fig. 4 shows the voltammogram obtained with a Ag flag electrode. When the potential was swept in the negative

Table I. The transport rate of SiCl_4 by the vapor transport method.

Exp. #	Temperature of SiCl_4 T/K	Vapor pressure of SiCl_4 $P_{\text{SiCl}_4}/\text{atm}$	Ar flow rate at 298 K $f_{\text{Ar}}/\text{mL min}^{-1}$	Reaction time t/min	Weight of SiCl_4 / g			Transport rate $v_{\text{SiCl}_4}/\text{mol min}^{-1}$
					Before reaction $W_{\text{SiCl}_4, \text{bef}}$	After reaction $W_{\text{SiCl}_4, \text{aft}}$	Transported ^b $W_{\text{SiCl}_4, \text{trans}}$	
# VT-1	293	0.257	20	50	250.55	248.12	2.43	2.86×10^{-4c}
Calculated	293	0.257	20	50	—	—	—	2.83×10^{-4d}
# VT-2	293	0.257	20	310	256.00	241.10	14.90	2.83×10^{-4c}
Calculated	293	0.257	20	310	—	—	—	2.83×10^{-4d}

$$^a P_{\text{SiCl}_4} = 10^{\left(4.0977 - \frac{1200}{T-37}\right)}$$

$$^b W_{\text{SiCl}_4, \text{trans}} = W_{\text{SiCl}_4, \text{bef}} - W_{\text{SiCl}_4, \text{aft}}$$

$$^c v_{\text{SiCl}_4} = \frac{W_{\text{SiCl}_4, \text{trans}}}{M_{\text{SiCl}_4} \cdot t}$$

$$^d v_{\text{SiCl}_4} = \frac{P_0}{RT} \cdot f_{\text{SiCl}_4} \cdot 10^{-6} = \frac{P_0}{RT} \cdot \frac{P_{\text{SiCl}_4}}{1 - P_{\text{SiCl}_4}} \cdot f_{\text{Ar}} \cdot 10^{-6}$$

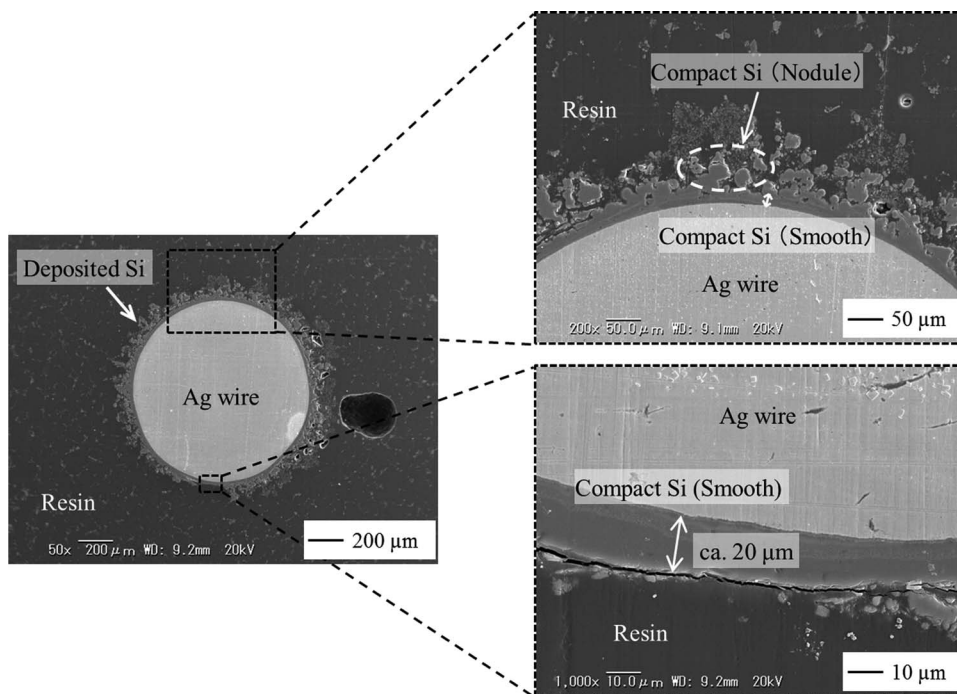


Figure 5. Cross-sectional SEM images of the sample obtained by the galvanostatic electrolysis of a Ag wire electrode at -155 mA cm^{-2} for 20 min in molten KF–KCl at 923 K after the introduction of SiCl_4 .

direction, a cathodic current peak is observed at 0.57 V vs. K^+/K , which corresponds to the deposition of Si.¹³ Additionally, a small cathodic current shoulder is observed at ~ 0.8 V, which is likely caused by the reduction of impurities. The voltammogram was compared with one that was previously obtained for the melt after the addition of 2.0 mol% K_2SiF_6 , as indicated by the broken curve in Fig. 4. The corresponding peak current densities for Si deposition are -1.742 A cm^{-2} and -1.521 A cm^{-2} in the solid curve (SiCl_4) and the broken curve (K_2SiF_6), respectively. Since the peak current density is proportional to the Si ion concentration,¹³ we estimated that the concentration of SiF_6^{2-} ions was 2.30 mol%. Thus, a melt with the optimum Si ion concentration (2.0–3.5 mol%) for the electrodeposition of compact films was successfully prepared.

The dissolution efficiency of SiCl_4 (2.30 mol% dissolved) was calculated to be 80% of the supplied amount (2.86 mol%). In contrast, the supplied SiCl_4 scarcely dissolved into the melt in the molten LiCl –KCl system at 723 K.¹⁹ Notably, we achieved a high dissolution efficiency even when a simple pipe with an inner diameter of 5 mm was used for bubbling. We expect that the time between SiCl_4 gas contacting and reacting with the KF–KCl molten salt was very short in our experimental system.

The high dissolution rate of SiCl_4 to the melt demonstrates that the use of SiCl_4 and a KF–KCl molten salt as the Si source and electrolyte, respectively, for Si electrodeposition is highly feasible. The high reactivity is explained by the large thermodynamic driving force of the reaction between SiCl_4 and KF, as shown by the thermodynamic calculation in Fig. 3 and Eq. 7. The use of a porous gas bubbler to produce finer bubbles is expected to improve the dissolution efficiency.

Electrodeposition of Si.—Since the voltammetry suggested the existence of some impurities in the melt, pre-electrolysis was carried out to remove them. After electrolysis at 0.95 V vs. K^+/K for 88 min, a black deposit was obtained on a Ag wire electrode. The deposit was found to consist mainly of iron metal by EDX. A small leakage in the gas supply system would lead to the reaction of SiCl_4 and moisture to form SiO_2 and hydrogen chloride. The hydrogen chloride gas probably corroded a stainless-steel connector between the PFA tube and the graphite pipe, introducing iron chlorides into the molten salt.

After pre-electrolysis, the electrodeposition of Si was carried out by galvanostatic electrolysis at -155 mA cm^{-2} for 20 min. Figure 5 shows cross-sectional SEM images of the obtained specimen. A compact Si film is observed on a Ag substrate. This result confirms the feasibility of using SiCl_4 gas as a Si source for Si deposition.

However, a smooth morphology is only observed near to the substrate, and the deposits are granular in the outer layer. Such a morphology is different from the deposit obtained with similar concentrations of Si ions in a KF–KCl– K_2SiF_6 molten salt (2.0–3.5 mol% K_2SiF_6).¹⁴ The main factor for this morphological difference is suggested to be the difference in the molar fractions of the F^- and Cl^- ions. Table II compares the anionic fraction of the melt after the addition of 2.00 mol% K_2SiF_6 and the introduction of 2.30 mol% SiCl_4 into a eutectic KF–KCl melt. Here, it is assumed that Si(IV) ions exist in the form of SiF_6^{2-} because of the higher affinity of fluorine and silicon than that of chlorine and silicon as discussed in Thermodynamic calculation section, and that the other ions exist as free ions. When 2.00 mol% of K_2SiF_6 is added to the melt, the anionic fraction of free F^- ions is 44.1% which is comparable to that of Cl^- ions (53.9%). However, when SiCl_4 gas is supplied to the KF–KCl molten salt, an exchange reaction between F^- ions and Cl^- ions occurs. Thus, the anionic fraction of Cl^- ions (66.0 %) increases to become twice that of the F^- ions (31.6 %). In previous studies, a compact and smooth Si layer was electrodeposited in pure fluoride molten salts.^{20–22} Thus, the high ratio of Cl^- ions in the present experiment is likely to cause the observed granular morphology. The influence of the anionic fraction on the morphology of Si deposit will be investigated in the future.

Table II. The anionic fraction of the melt after the addition of 2.00 mol% K_2SiF_6 and the introduction of 2.30 mol% SiCl_4 into KF–KCl molten salt.

Si source	Anionic fraction/%		
	F^-	Cl^-	SiF_6^{2-}
K_2SiF_6 (2.00 mol%)	44.1	53.9	2.0
SiCl_4 (2.30 mol%)	31.6	66.0	2.4

Conclusions

The dissolution of SiCl_4 gas into a KF-KCl molten salt and the electrodeposition of Si from the melt were investigated. A mixed Ar-SiCl_4 gas containing 14.90 g of SiCl_4 was introduced by a gas transport method into a eutectic KF-KCl melt (200 g) at 1023 K. Cyclic voltammetry indicated that a melt with 2.30 mol% of Si ion concentration was produced. The dissolution efficiency of SiCl_4 was calculated to be 80% from measurements of the amount of SiCl_4 that was supplied (2.86 mol%) and that dissolved (2.30 mol%). A Si film was deposited on a Ag substrate at 923 K by galvanostatic electrolysis at -155 mA cm^{-2} for 20 min. Cross-sectional SEM observation confirmed that a compact Si deposit was achieved. The observed granular morphology may have been caused by the molar ratio of F^- and Cl^- anions, which will be confirmed in future investigations.

Acknowledgments

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